

Abstract No. Yang0276

Investigation of the Local Structure of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ Cathode Material during Electrochemical Cycling by X-ray Absorption and NMR Spectroscopy

W-S. Yoon (SUNY, Stony Brook), X.Q. Yang (BNL), M. Balasubramanian (BNL), J. McBreen (BNL), and C. Grey (SUNY, Stony Brook)

Beamline(s): X18B

Introduction: Layered lithium nickel manganese oxides have recently been shown to be promising positive electrode materials for use in lithium-ion rechargeable batteries. Ohzuku et al.¹ showed that lithium nickel manganese oxide represents a possible alternative to LiCoO_2 for advanced lithium batteries, in terms of its operating voltage, capacity, cycleability, safety, and materials economy. Lu et al.² reported that $\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$ with $x = 1/3, 5/12$, or $1/2$ can be cycled between 2.0 and 4.6 V to give a stable capacity of about 200, 180, or 160 mAh/g, respectively, at room temperature. The DSC results showed good safety characteristics. In this work we apply a combination of in situ XAS and ^6Li MAS NMR spectroscopy to examine the $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode system and probe the electronic and local structure around the Mn/Ni and Li atoms during the first charge and discharge processes. We establish the major charge compensation mechanisms in the $\text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2$ electrode system during electrochemical cycling and show that these materials are more disordered than implied by their nominal composition.

Methods and Materials: $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powders were synthesized by reacting stoichiometric quantities of a coprecipitated double hydroxide of manganese and nickel with lithium hydroxide at 900 °C for 24 h in O_2 . Cathode specimens were prepared by mixing the $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powders with 10wt.% acetylene black and 10wt.% PVDF(poly-vinylidene fluoride) in NMP(n-methyl pyrrolidone) solution. 1M LiPF_6 in a 1:1 ethyl carbonate:dimethyl carbonate (EC:DMC) solution was used as the electrolyte. The cell was assembled in an argon-filled glove box. Samples for the NMR experiments were prepared by using an electrochemical cell. The cell was disassembled and the electrodes were washed with tetrahydrofuran prior to packing the samples into the NMR rotors. XAS measurements were performed in the transmission mode at beamline X18b of the National Synchrotron Light Source.

Results: We have investigated the evolution of the local electronic and atomic structure of the $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode using *in situ* Mn and Ni K-edge XAS and ^6Li MAS NMR techniques, during the first charge and discharge process. From the Mn and Ni K-edge XANES results, we conclude that the charge compensation when charging between 2 and 4.6 V is achieved mainly by the oxidation of Ni^{2+} to Ni^{4+} ions, while the manganese ions remain mostly unchanged in the Mn^{4+} state. The EXAFS results are consistent with these conclusions. When discharging at low voltage plateau (~1 V), however, the charge compensation for the Li-ion intercalation process is achieved via reduction of Mn^{4+} .

Conclusions: The ^6Li MAS NMR results of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ at different charge states reveal that Li is found not only in the Li layer but also in the $\text{Ni}^{2+}/\text{Mn}^{4+}$ layers, primarily in an environment surrounded by 6 Mn^{4+} as in Li_2MnO_3 . All the Li^+ in the $\text{Ni}^{2+}/\text{Mn}^{4+}$ layers are removed on charging to form $\text{Li}_{0.4}\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, the residual Li^+ occupying sites near nickel in the lithium layers.

Acknowledgments: We thank Syed Khalid for his help at Beam Line X18b at NSLS. The work performed at SUNY Stony Brook was supported by the National Science Foundation (DMR 9901308) and SUNY Stony Brook, via a joint USB/BNL grant. The work carried out at BNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division, USDOE under Contract Number DE-AC02-98CH10886.

References:

1. T. Ohzuku and Y. Makimura, Chemistry Letters (2001) 744.
2. Z. Lu, D. D. MacNeil, and J. R. Dahn, Electrochem. Solid-State Lett. 4 (2001) A191.